



# Physical Equilibria and all that

Regrades Due FRIDAY!

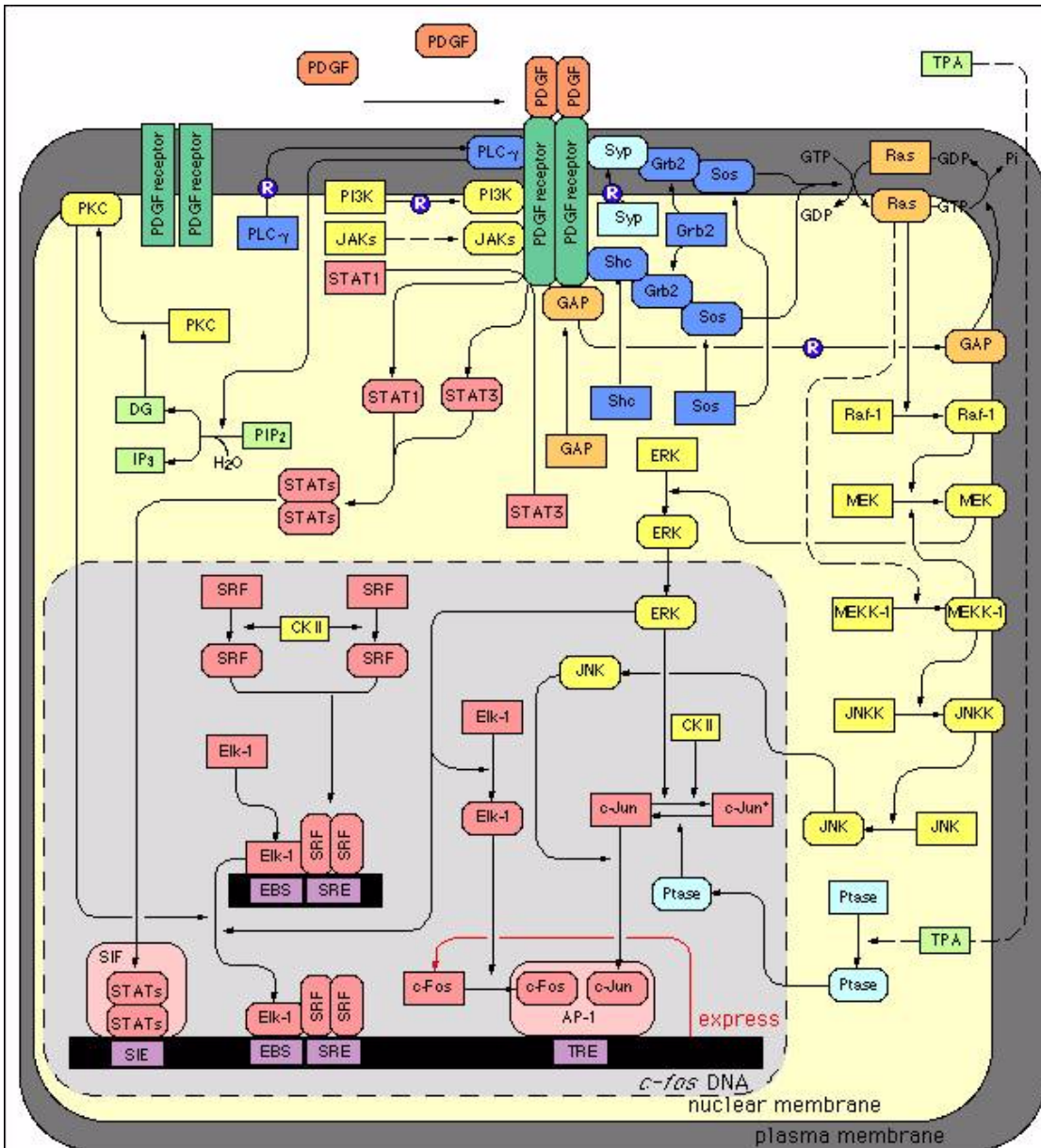
RESULTS will be given in class Monay,

Raoult's law

Henry's law

Scatchard Plots

# Platelet-Derived Growth Factor Pathway.



We were talking about

Physical Equilibria

Colligative Properties

The effect of binding on equilibria



For phase equilibria we know the following:

For a single component:

$$\mu_{\text{phase1}} = \mu_{\text{phase2}} = \mu_{\text{phase3}}$$

Which implies that

$$\mathbf{a}_{\text{phase1}} = \mathbf{a}_{\text{phase2}} = \mathbf{a}_{\text{phase3}}$$

provided that *we use the same standard state in all phases!*

If we have more than one “independent” component then:

$$\mu_A(\text{phase 1}) = \mu_A(\text{phase 2}) = \mu_A(\text{phase 3})$$

$$\mu_B(\text{phase 1}) = \mu_B(\text{phase 2}) = \mu_B(\text{phase 3})$$

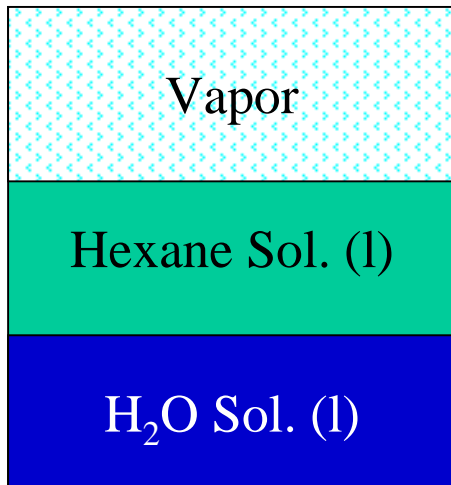
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# Phase Equilibria

What happens when you try and get a hydrophilic drug across a cell membrane?

In general, unless there is a specific active transport process, it is very difficult. But you can always get some in since there is usually some partition between phases.

Let's consider a simple system composed of  $\text{H}_2\text{O}$ , Hexane in both liquid and gas form.

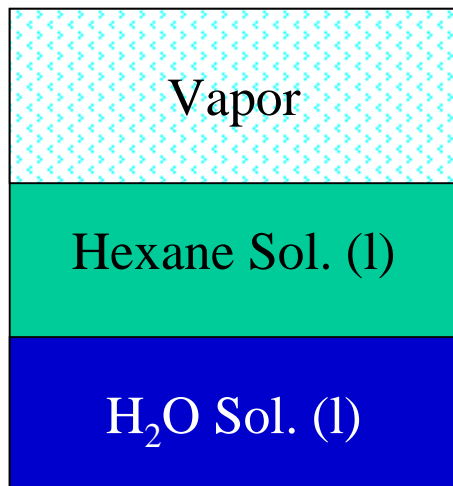


If we wait long enough this system will come to equilibrium.

We find that there is  
some hexane in the water.  
some water in the hexane  
a mixture of water and hexane gas.

We know that the chemical potentials for each species in all phases of this system are equal.

# Phase Equilibria



If we use the same standard state for all phases then the fact that

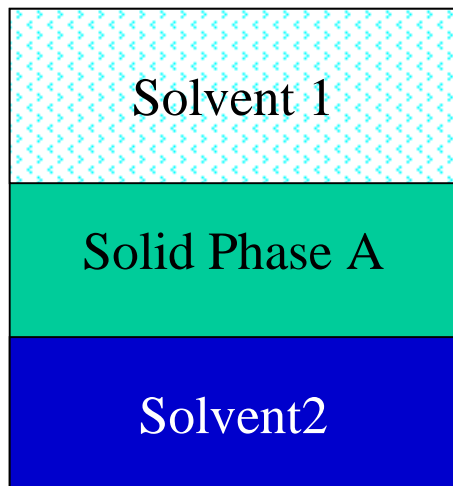
$$\mu_{\text{hexane (l)}} = \mu_{\text{hexane (aq)}} = \mu_{\text{hexane (g)}}$$

implies that the activity of hexane in all three phases is the same.

But we know the concentrations are different!

So what's different?

# Phase Equilibria



Now what?

Well, if we let it come to equilibrium and assume that there is a vast excess of the solid phase then we know something strange:

$$\mu_{A \text{ (solvent 1)}} = \mu_{A \text{ (solvent 2)}} = \mu_{A \text{ (solid)}}$$

So we can directly calculate the  $\Delta\mu$  for transferring A from one solvent to the other, right?

We measure the activity of our solute in the two phases and since the  $\mu^\circ$ 's are different for the two solute standard states (which have a solute activity of 1), we can calculate this difference by plugging in our measurements.

At equilibrium we know

$$\mu_A(l, \text{soln}) = \mu_A(g, P_A)$$

$$\mu_A^\circ(l, \text{pure}) = \mu_A^\circ(g, P_A^\circ)$$

Now we can derive a relation for the pressure of A above the solution:

$$\begin{aligned} \mu_A(l, \text{soln}) - \mu_A^\circ(l, \text{pure}) &= \mu_A(g, P_A) - \mu_A^\circ(g, P_A^\circ) \\ &= RT \ln(P_A/P_A^\circ) \end{aligned}$$

For an ideal gas the activity of the gas is simply

$$\mathbf{a_A(g) = P_A/P_A^\circ}$$

For the liquid-- the activity is

$$\mathbf{a_A(l) = \gamma_A X_A}$$

$P_A, P_B$

**Substance B  
Dissolved in  
Solvent A**



So for an ideal solution and ideal gas

$$RT \ln(\mathbf{a}_A(l)) = RT \ln(\mathbf{a}_A(g))$$

implies the two activities must be equal

$$\mathbf{a}_A(l) = \mathbf{a}_A(g)$$

$$X_A = P_A/P_A^\circ$$

Upon rearrangement we get Raoult's law

$$P_A = X_A P_A^\circ$$

Thus adding solute decreases the vapor pressure of A above solution.

Note that this is a *colligative* property!





It is worth, now, understanding the relationships among all the different types of concentration we talk about:

Molarity	-	$c$
Molality	-	$m$
Mole Fraction	-	$X$

Given that we have a solvent of molecular weight  $M$ , and a density,  $\rho$ , the relations are as follows:

$$X = M * m / 1000$$

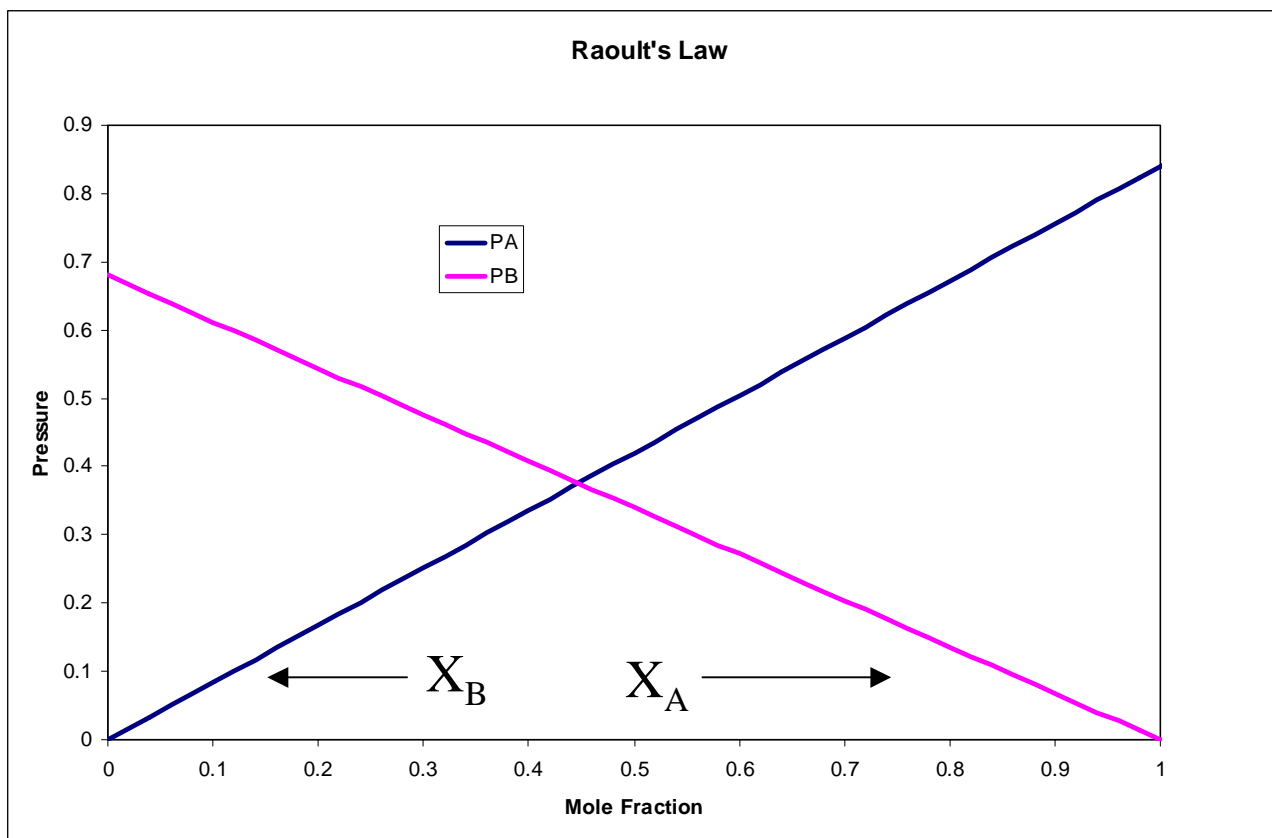
$$c = \rho * m$$



## Raoult's law

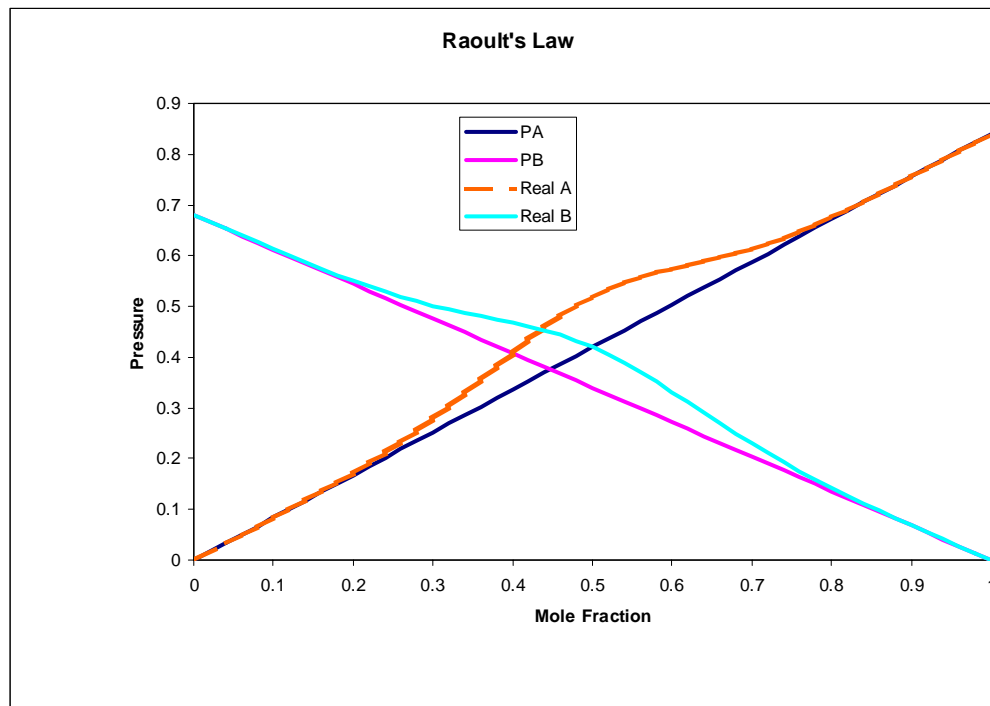
$$P_A = X_A P_A^\circ$$

A graph of this property is given by





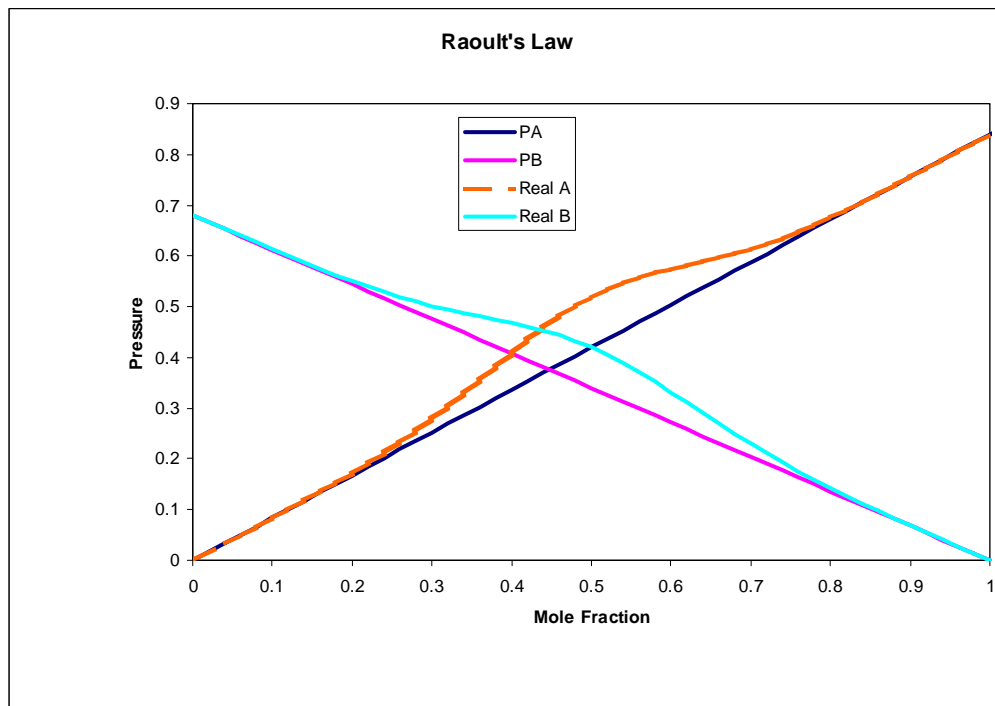
In the real case, we get deviations.



The case shown shows positive deviations from Raoult's Law.  
We can also have negative deviations.

If one component has negative deviations can the other component have positive ones?

Will the tangents to the non-ideal curves be the same at high and low ends?



Components will have same signed deviations!

Deviations result from interactions between solute and solvent.

Positive deviations means that the two components repel one another.

e.g.  $\text{CCl}_4$  and  $\text{CH}_4$

Mixing these two together increases their vapor pressure!

Are the deviations of the two components the same?

What would cause negative deviations?

Are the tangent slopes to the deviation at  $X=0$  and  $X=1$  the same?

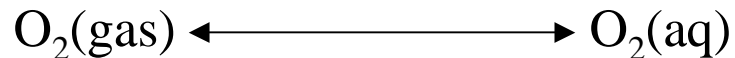


Now let's look at it from the solvent point of view. Here we are concerned with the solubility of a substance in a solvent.

You know that when we draw a glass of water there are bubbles in it. When you open a can of soda a great deal of gas escapes.

In the water case, are the bubbles the same as the bubbles when boiling?

In any case, air gets dissolved in the water. So we have the following equilibrium:



As you raise the temperature of the water more and more  $\text{O}_2$  comes out of solution.

Empirically, it is found:

$$P_B = X_B * k_B$$



This is **Henry's Law**

$$P_B = X_B * k_B$$

This is also a colligative property sort of....

It says, for example, that 5 times more oxygen will dissolve in H<sub>2</sub>O in equilibrium with pure O<sub>2</sub> than will dissolve in atmospheric O<sub>2</sub> (P<sub>O2</sub>= 0.2)!

What is the difference between this law and Raoult's law?

Well, for one, k<sub>B</sub> is dependent on the solvent.

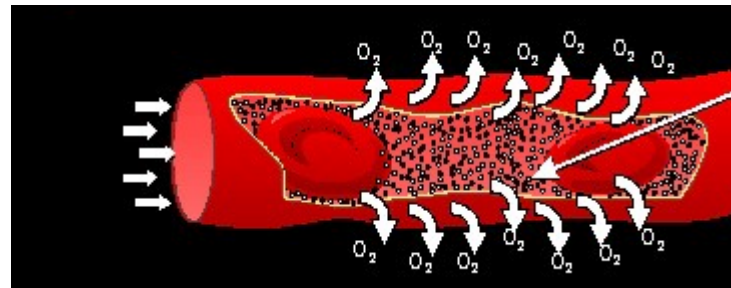


Example of importance:

When scuba diving to great depths the effective pressure on blood gases goes way up.

The divers are breathing a mixture high in  $O_2$  in a carrier gas of  $N_2$ .

Because of the high pressures, more of these gases dissolve in the blood than normal.



$O_2$  is actually used by the cells and expelled in  $CO_2$  back outside the diver. But  $N_2$  remains at high levels in the blood.

If a diver ascends too fast,  $N_2$ , catastrophically bubbles out of the blood, blocking capillaries and blood flow! This is called the bends!



Henry's Law Constants $k_B$ (atm) = $P_B/X_B$			
gas	0°C	25°C	37°C
He	133 $10^3$	141 $10^3$	140 $10^3$
CO	35 $10^3$	58 $10^3$	94 $10^3$
O <sub>2</sub>	26 $10^3$	43 $10^3$	51 $10^3$
Ar	24 $10^3$	39 $10^3$	46 $10^3$
CO <sub>2</sub>	0.72 $10^3$	1.61 $10^3$	2.16 $10^3$
C <sub>2</sub> H <sub>2</sub>	0.72 $10^3$	1.34 $10^3$	1.71 $10^3$

Note that as  $k_B$  increase, solubility decreases!

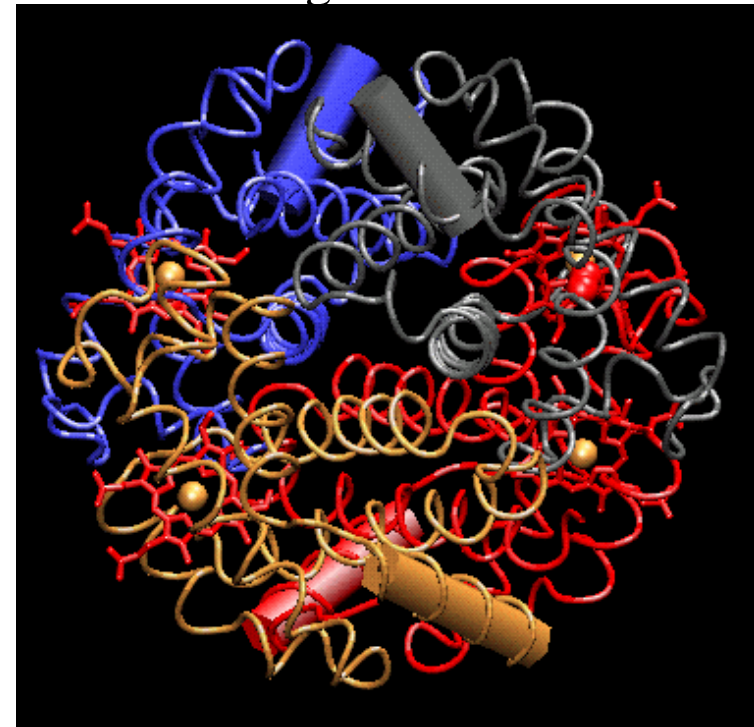
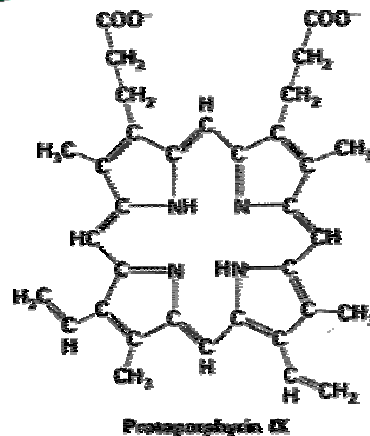
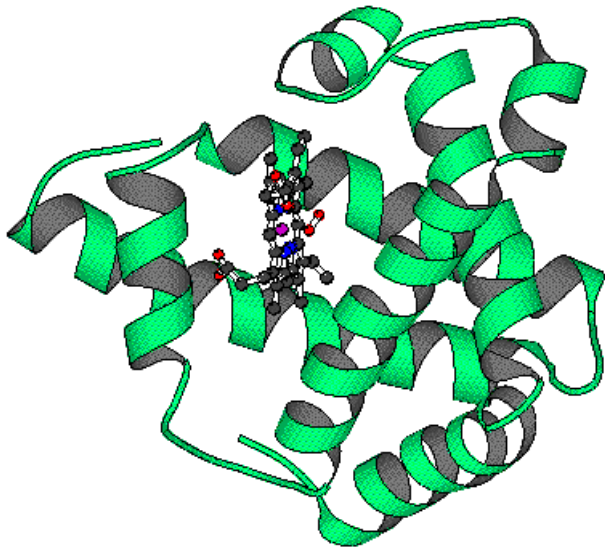
Note that at body temperature we only have 51 parts O<sub>2</sub> in 1000 in H<sub>2</sub>O!





We have developed strategies to do better!

- 1) Oxygen binding proteins: Myoglobin, Hemoglobin
- 2) Awesome transporters both molecular and geometrical





But sometimes they fail!

One way of dealing with this in infants is by using a breathable fluid!

Such a fluid is Perfluobromine:  $C_8F_{17}Br$

The solubility of  $O_2$  in PFB is:

57 ml/deciliter

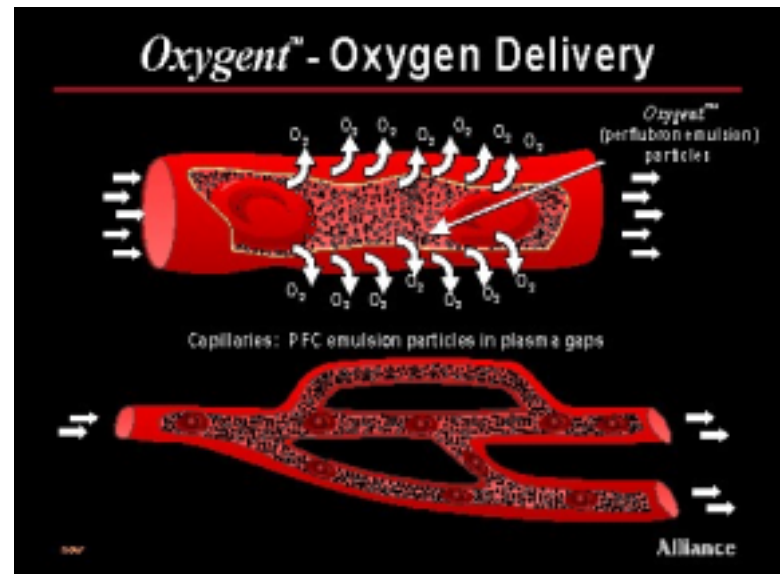
The solubility of  $O_2$  in saline is:

2 ml/deciliter

(Can you convert this to mole fraction?)

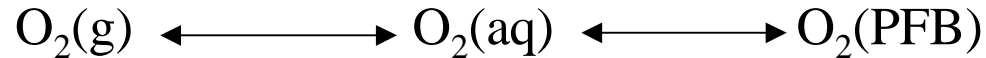
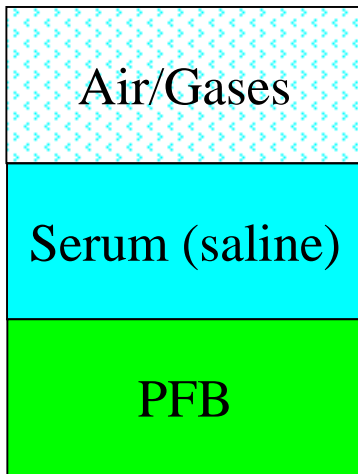
Thus this fluid delivers more  $O_2$  to the lungs:

This is nice, because  $O_2$  is not bound to anything, its just dissolved so that Hemoglobin can easily bind it into its pocket.



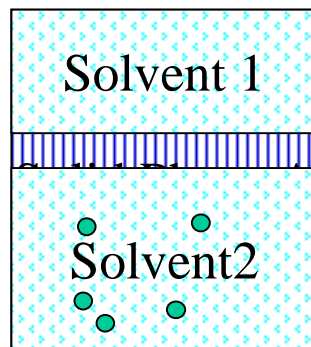


PFB is also high hydrophobic. When introduced into the blood there are three phases in equilibrium.



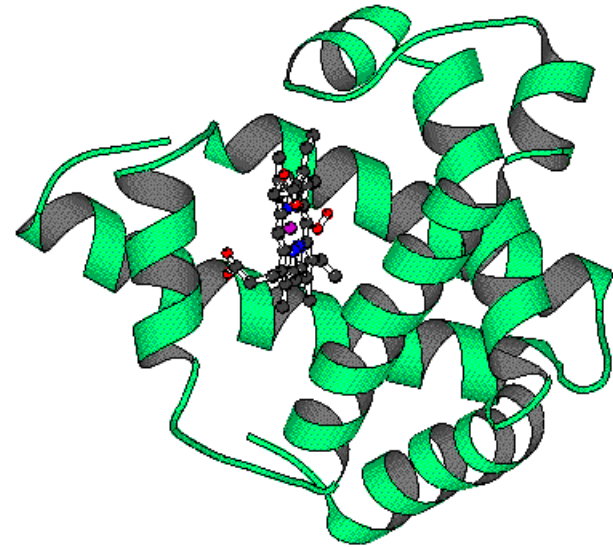
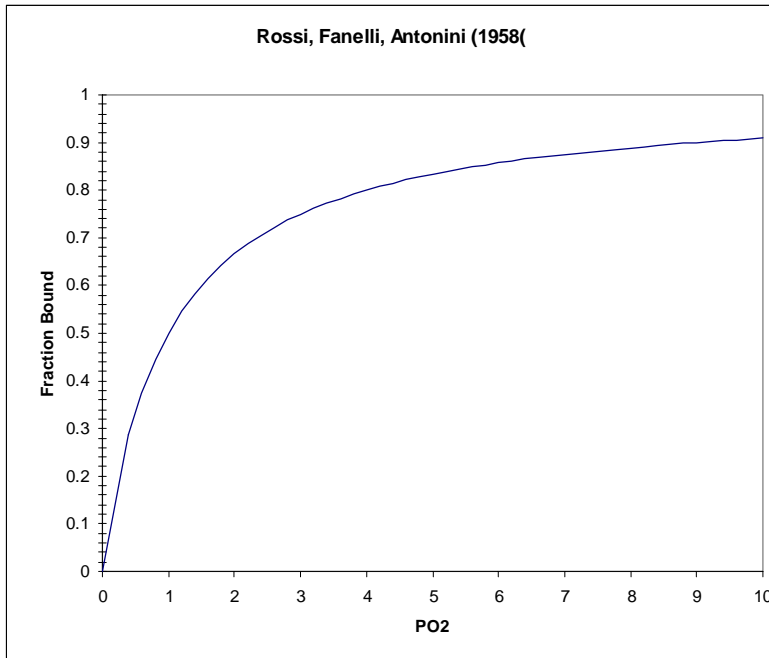
$$\mu_{\text{O}_2}(\text{g}) = \mu_{\text{O}_2}(\text{soln}) = \mu_{\text{O}_2}(\text{PFB})$$

What happens when I provide a substance in one phase that binds  $\text{O}_2$ ?



← Semi-permeable Membrane

● = a protein that can bind a solute dissolved in the solvents



$$\text{Total Myoglobin} = \text{Myo}_0 = \text{Myoglobin} + \text{Myo-O}_2$$

$$K = \frac{[\text{O}_2][\text{Myoglobin}]}{[\text{Myo-O}_2]}$$

$$\text{Myo}_0 = K[\text{Myo-O}_2]/[\text{O}_2] + [\text{Myo-O}_2]$$

$$[\text{Myo-O}_2]/\text{Myo}_0 = [\text{O}_2]/(K + [\text{O}_2])$$



Homework:

TSW 5.2, 5.3(a), 5.5, 5.6, 5.7, 5.9